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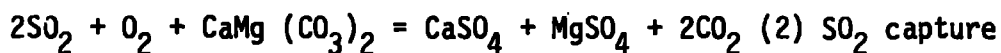
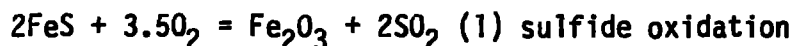
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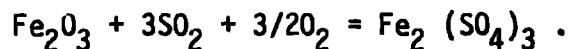
I. SULFUR AND NITROGEN IN OIL SHALE PROCESSING

This quarter we have continued working toward our goal of being able to predict the disposition of sulfur and nitrogen given the operating conditions for any oil shale process. Our emphasis is above-ground retorting where retorted-shale combustion is utilized for the heat supply for retorting. Retorted shale contains both mineral sulfur (FeS) and organic sulfur (in the char). We have previously reported that the combustion of retorted shale does not release SO₂ if the combustion temperature is sufficiently high (>525°C) so that the reaction between SO₂ and dolomite is rapid. The net reaction may be a combination of the following two reactions:



This quarter we have studied the rate of SO₂ capture by oxidized oil shale and the relation between the fraction of carbonate reacted (sulfated) and the rate of reaction. Measurements were made of the decrease in SO₂ concentration in a gas (2% O₂, 0.1% SO₂ balance N₂) as it passed through a heated bed of granular oxidized oil shale. The rate of reaction was calculated from the decrease in SO₂ concentration, and the transit time of the gas through the bed. We found that the rate is a complex function of bed temperature and the length of an experiment suggesting that more than one reaction is taking place which removes SO₂. This is confirmed by the fact that the rate of CO₂ release was less than the rate of consumption of SO₂.

(According to reaction 1 the rates should be equal.) We found that when the inlet concentration of SO_2 was decreased to zero, after a period of time during which the SO_2 has been scrubbed, the concentration of SO_2 down stream from the bed also fell to zero, but CO_2 was found in the exit gas for some time after. It appears that iron oxide (Fe_2O_3) in the oxidized shale is also removing SO_2 and the reaction is:



When the inlet concentration of SO_2 is reduced to zero the iron sulfate becomes unstable and SO_2 is released by the iron sulfate to continue to attack carbonate, thereby releasing CO_2 .

Our work on nitrogen was reported to the Rocky Mountain Fuels Society and to the Fuels Division of the American Chemical Society this quarter. (See tabulated reports and presentations).

We have confirmed the important concentrations of inorganic nitrogen in oil shale by means of I.R. adsorption. We have learned that oil shale nitrogen is distributed in solid, liquid and gaseous products of retorting, and how increasing retorting temperatures or time increases the concentration of gaseous nitrogen species, probably ammonia, at the expense of nitrogen in the solid retorted shale. Under the same range of conditions the nitrogen content of the oil remains nearly unchanged. Oxidation of retorted shale results in the release of NO (nitric oxide) and we have found that these NO emissions can be significantly reduced by stopping the oxidation of retorted shale before all the char is consumed.

II. INITIAL OPERATION OF THE SOLIDS-RECYCLE RETORT SYSTEM

In the solids recycle system, hot, burned shale serves as the heat source for pyrolysis of raw shale. In the LLNL equipment, mixing of the burned shale with the raw shale and pyrolysis of the raw shale is accomplished in a dense phase fluidized bed. Figure 1 is a schematic of the system. Principal components in the recycle loop are the mixer-pyrolyzer, surge tank, lift pipe, and combustor. All of these components and the interconnecting pipes are fabricated of stainless steel, are insulated and have electrical heaters attached to the outer steel surface under the insulation. The power from each of the heaters is almost exactly equal to the heat flow through the insulation at each point so that there is no heat flow through the steel walls.

In the first operation of the equipment, designated run R-1, the pyrolyzer was fluidized by preheated nitrogen. Lift gas and combustion gas were preheated air. Raw shale feed rate was 960 gm/min. The ratio of burned-to-raw shale entering the pyrolyzer was 3.8. Table 1 shows the mass balance for run R-1. The 3% loss of material indicated on Table 1 is probably due to dust in the combustion gas discharged to the atmosphere. Although this gas passed sequentially through two cyclones, there was observable dust in the discharge. Table 2 shows the organic carbon balance for R-1. Figure 2 shows a typical temperature profile of the recycle material from the pyrolyzer exit to inlet. Oil yield as a fraction of assay is not yet known since the report of assay has not yet been received.

In the second operation, run R-2, the fluidization gas was the pyrolysis gas from the discharge of the oil condensers. Since this gas has substantially lower viscosity than nitrogen, a higher flow rate was used for R-2 than for R-1. This higher gas flow rate resulted in an overload of the coolers in the oil condensers, resulting, in turn, in the loss of oil. For this reason, a balance on organic carbon cannot be obtained for R-2. Cooling capacity in the condensers has been greatly increased so that loss of oil will be avoided in future runs.

III. SULFUR GAS ANALYSIS BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

The TQMS was used to analyze grab samples from the pyrolysis section of the solids-recycle retort system during retort runs R-2 and R-3. These grab samples were analyzed for H_2S , mercaptans, thiophenes, sulfides, disulfides and COS within one hour of sampling to prevent loss of sulfur species on the container walls. Table 3 shows the results for these retort runs.

In retort run R-2, H_2S was reduced from an expected 20,000 ppm (for Fischer assay) to a few ppm and methanethiol was reduced from 130 ppm to 5 ppm. In retort run R-3, the H_2S was roughly 25 times greater at ~50 ppm than in R-2, but still represented a significant reduction in expected amounts of H_2S .

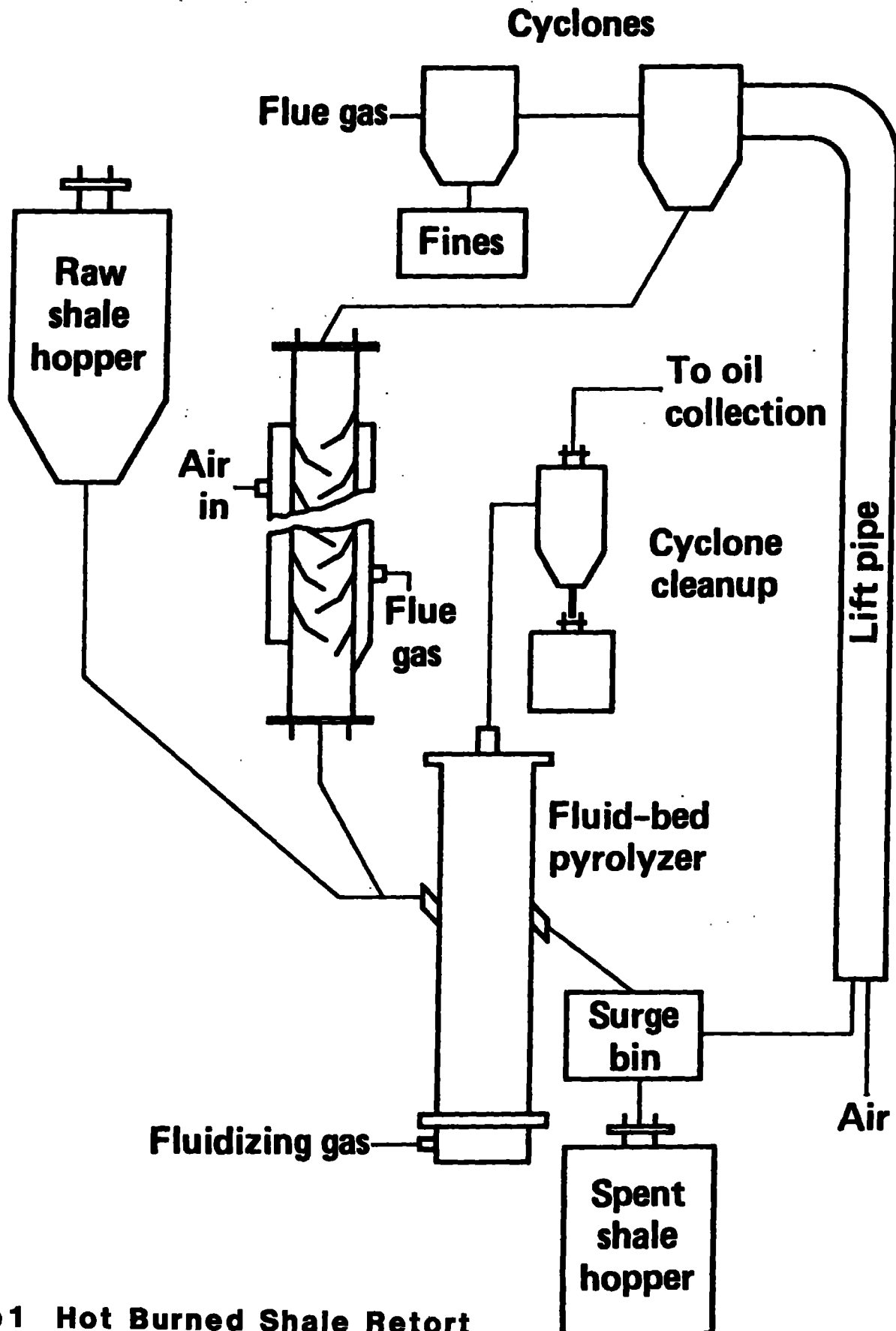


Figure 1 Hot Burned Shale Retort

FLUID BED PYROLYZER RUN R-1
RECYCLE SOLIDS TEMPERATURE PROFILE

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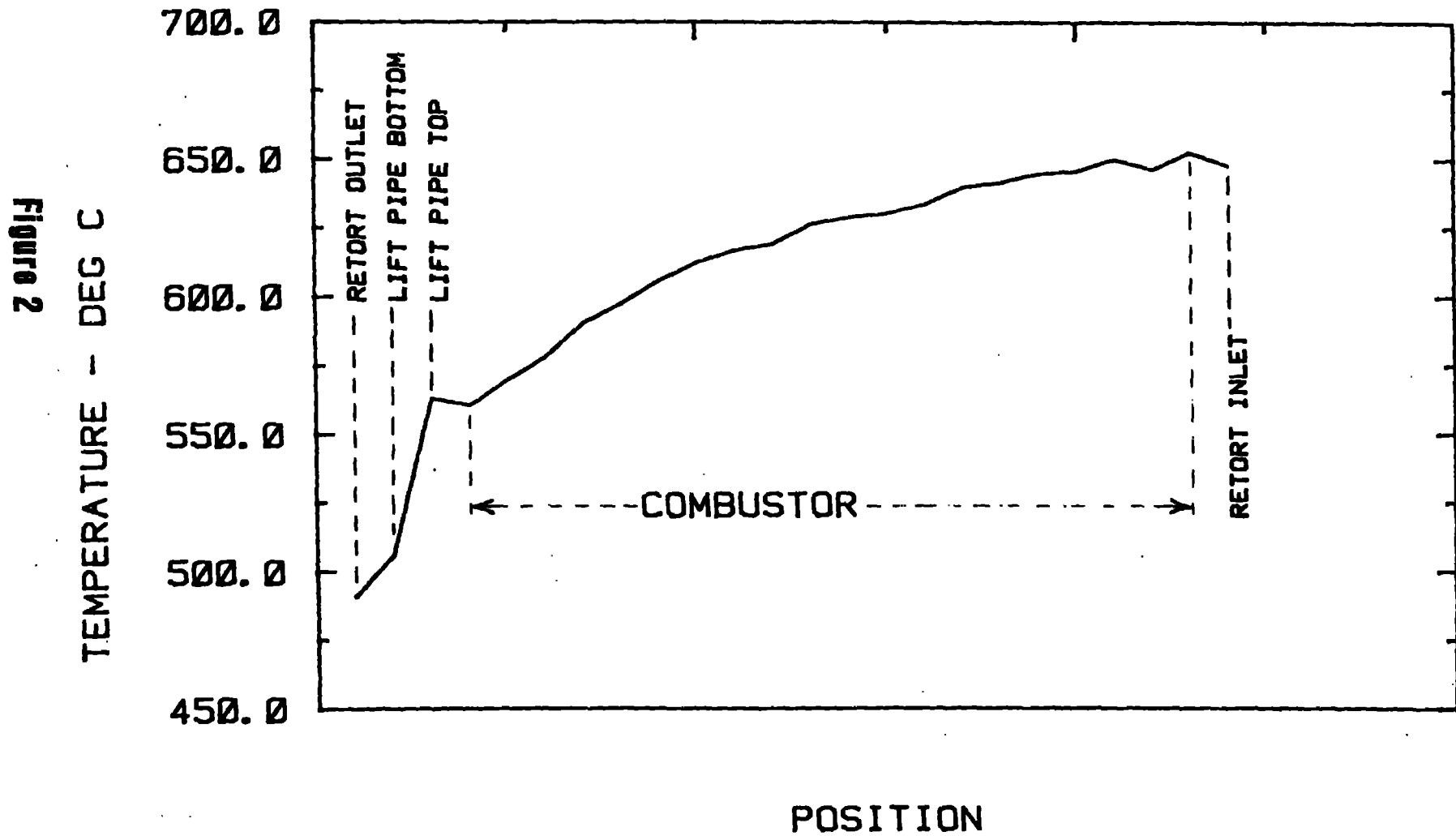


TABLE 1 R-1 Mass Balance - gm/min

In-Raw Shale	960.0
Out	
Solids	
Pyrolyzer discharge	487.8
Cyclones before oil collection	227.5
Flue gas cyclones	87.6
Dust in oil	7.5
Liquids	
Oil	58.9
Water	17.9
Gases	
Pyrolysis gas	23.3
Carbon in flue gas	20.5
Out/In = 0.970	

TABLE 2 R-1 Organic Carbon Balance - gm/min

In-Raw Shale	95.4
Out	
Solids	
Pyrolyzer discharge	4.8
Cyclones before oil collection	6.6
Flue gas cyclones	0.8
Dust in oil	0.4
Oil	49.2
Gases	
Pyrolysis gas	13.0
Carbon in flue gas	20.5
Out/In = 0.998	

Such a dramatic reduction in H_2S for the recycle retort was expected based on previous lab-scale experiments. These were done on-line on the TQMS using a Fisher assay-like pyrolyzer, and shale samples to which a variety of minerals common to burned shale were added (dolomite, $CaCO_3$, ankerite, CaO , siderite, Fe_3O_4 and Fe_2O_3). A significant reduction in sulfur gases resulted, particularly when an iron oxide or siderite was added.

The conditions of the recycle retort runs allowed a much more complete mixing of solids and gases than did the lab experiments and so there was a more complete removal of the sulfur gases than was experienced in the laboratory scale pyrolysis experiments; but, the trends predicted by the on-line, Fischer assay-like apparatus held true. We had predicted that the iron oxides found in the burned shale would react with H_2S and most trace sulfur containing gases with the exception of the thiophenes. This is exactly what was seen from the retort pyrolysis gas samples run on TQMS. Even the ratio of thiophene to methyl thiophene (1:2) was very similar to that found in our laboratory experiments.

The dimethyldisulfide levels were 5 times lower in R-3 than in R-2. With the exception of mercaptans and H_2S , the trace sulfur gases remained at about the same level in both runs. Thiophenes were not reduced in either the lab scale experiments or in the retort runs, R-2 and R-3.

The difference in the apparent H_2S concentration between the two runs may be due to a progressive decrease in the tendency of the sample bottles and the retort system itself to react with H_2S . (In a subsequent run the H_2S concentration was found to decrease when the circulation of the pyrolysis gas was stopped.)

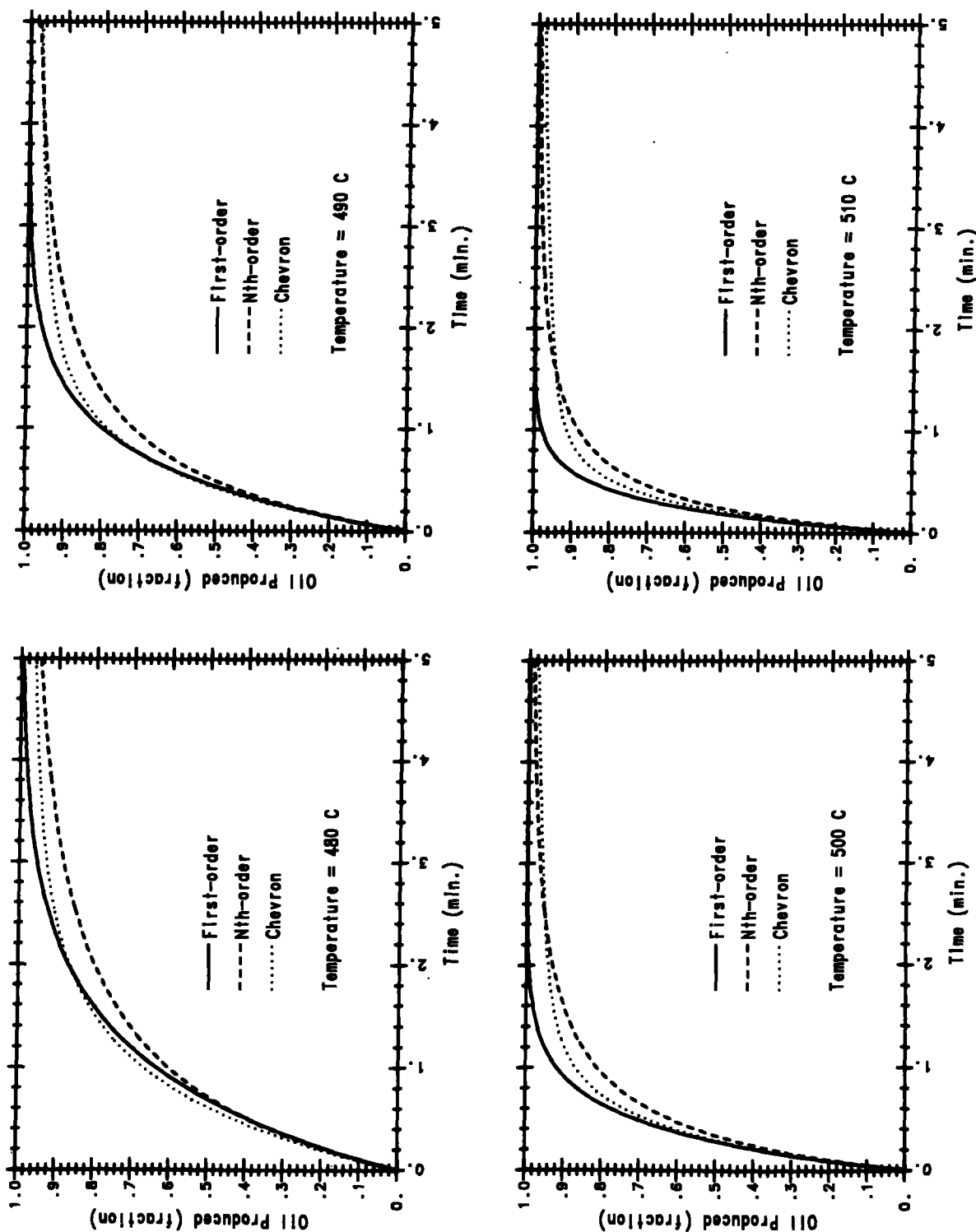
Table 3. Sulfur containing gases in ppm as determined by triple quadrupole mass spectrometry

Date of Retort	R-2				R-3				
	28-Mar-84				4-Apr-84				
Time Into Experiment	:01	:14	:34	:43	:02*	:03	:15	:31	:35
Hydrogen sulfide —	3.	1.	2.	1.	49.	36.	51.	63.	48.
Methanethiol —	5.	2.	1.	1.	7.	7.	8.	8.	7.
Ethanethiol —	4.	1.	<1.	<1.	3.	3.	3.	3.	3.
Propanethiol —	1.	<1.	<1.	<1.	1.	2.	1.	1.	1.
Dimethyl sulfide —	<4.	<4.	<4.	<4.	<4.	<4.	<4.	<4.	<4.
Dimethyl disulfide —	9.1	2.3	1.0	0.2	0.1	0.3	0.3	0.3	0.2
Carbonyl sulfide —	4.	2.	<1.	<1.	4.	4.	3.	3.	3.
Carbon disulfide —	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.
Thiophene —	28.	18.	5.7	6.1	7.8	14.	15.	14.	16.
Methyl thiophene —	44.	31.	10.	10.	5.4	25.	26.	23.	25.

* Sample in Mylar bag, all others in stainless steel bottles

IV. RETORT MODELING

In order to process oil shale efficiently in aboveground retorts, it is desirable to use the minimum residence time in the pyrolyzer that will give the desired conversion. Comparisons of the various experimental determinations of the kinetics for kerogen pyrolysis are shown in Figure 3 at various fixed temperatures between 480°C and 510°C. Marked differences can be seen at each temperature. For example, at 500°C the calculated residence time to give 98% of the maximum oil yield was 1.5 minutes for the first-order reaction reported by Campbell for non-isothermal experiments at a relatively low heating rate of 2°C/min, 4 minutes for the 1.4-order reaction derived by Braun and Burnham from fluid-bed data at heating rates probably in excess of 1000°C/min, and 5 minutes for the more complex, multi-reaction mechanism derived by Chevron, also from fluid-bed data at high heating rates. These



**Figure 3 Degree of kerogen pyrolysis as a function of time
at temperatures of 480 to 510 C.**

discrepancies must be resolved to have adequate predictive capability in our retort models. Additional kinetic experiments at high heating rates would be particularly relevant.

Our computer model for the LLNL cascading-bed retort system was modified to include a surge bin for the shale passing from the pyrolyzer to the lift pipe. The complete system is now done as an iterative sequence of reactor calculations, using our dynamic, moving-bed, retort model to separately simulate a pyrolyzer, a surge bin below the pyrolyzer, and a cascading-bed combustor above the pyrolyzer. The loop is closed by a steady-state model for a lift pipe. A major modification was also accomplished in the pyrolyzer model to allow particle-size-dependent velocities through the reactor. This is particularly important in simulating the LLNL two-stage fluidized-bed retort, in which the fines move more than a factor of 2 faster than the coarsest particles. Changes were also made in our lift-pipe model to allow certain parameters to be fixed for a given calculation (e.g., lift-pipe diameter, air flow rate). Previously, for exploratory studies, the model was allowed to determine optimum values of these parameters, rather than to use specified values. The complete model for the cascading-bed retort system is now ready for application to the specific conditions of our experimental setup.

A comprehensive mathematical model is being developed for the chemical reactions in a single particle of retorted oil shale in a combustor. Oxidation of char (CH_xN_y) and iron sulfide, reduction of NO by char, capture of SO_2 by dolomite, and thermal decomposition of dolomite are included. Intraparticle diffusion of O_2 , SO_2 , NO, and CO_2 is also included. The model will be used to interpret data from chemical kinetics experiments. More reactions will be added to the model if indicated by comparisons with experimental data. This comprehensive model will also be

used in deriving approximate models for the combustion reactions that can more readily be incorporated in the global reactor models for a lift-pipe combustor or for a cascading-bed combustor.

Our moving-bed retort model was used to investigate the effects of changes in the hot-gas input rate for a hot gas retort using external combustion. The Union B retort is one of this type. First, a base inlet-gas flow rate at 482°C was established, such that only 1% of the kerogen was unpyrolyzed in the outlet shale at 477°C. A 10% and 20% decrease in the gas flow rate caused the unpyrolyzed kerogen in the outlet shale to increase to 14% and 27%, respectively. Furthermore, the outlet shale temperature decreased to 468 and 464°C, respectively. Thus, minor non-uniformities of the inlet-gas flux across the top of the shale could have pronounced effects on the degree of pyrolysis of the outlet shale, on the physical properties of the oil generated, and on the physical properties (especially cohesion) of the shale at the top of the retort. The calculations also illustrate that, even with a high inlet gas flow rate, these same undesirable effects are necessarily present during start-up of the retort, if the hot-gas flow and the bed movement are simultaneously started in a retort loaded with raw shale at ambient temperature (i.e., no preheating of the shale bed before upward movement is started). On the other hand, if the shale bed is preheated (even for as short a period as 14 minutes) before upward movement is started, the outlet shale is fully retorted initially and decreases gradually to the steady-state value. The results of this study are summarized in Figure 4.

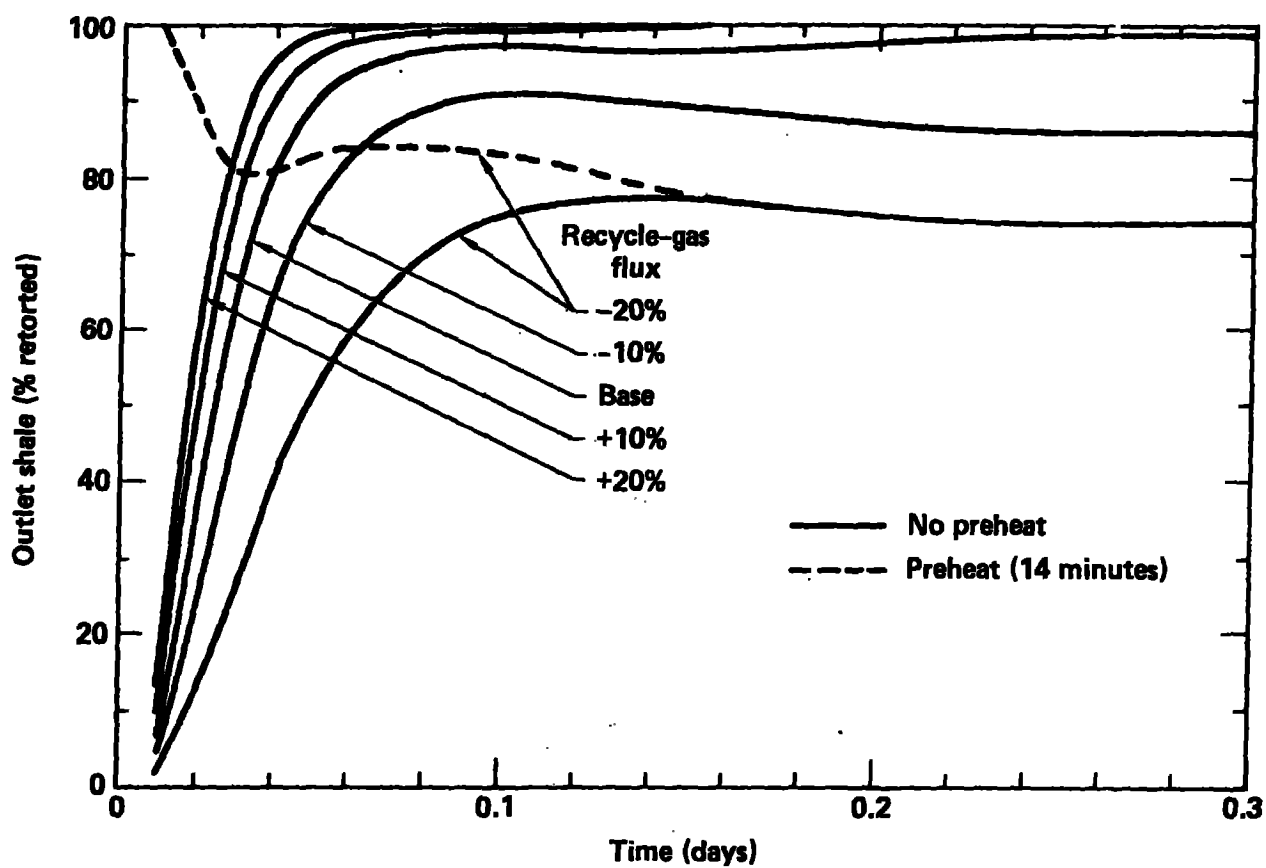


Figure 4. The degree of pyrolysis of the outlet shale as a function of recycle-gas flux, start-up time, and preheat time.

Our previous calculations for the Union-B retorting process assumed that a coal-burning furnace would be used to heat the recycle gas. Alternatively, the heat could be supplied by burning product gas and, if necessary, some product oil. New calculations for a 50,000 bbl/day plant using 30 gal/ton shale illustrate that all of the gas product (C_4 - minus) and nearly 3% of the oil product (C_5 - plus) would have to be burned (assuming 80% efficiency for the heat transfer from the flue gas to the recycle gas). This increased the amount of raw shale processed by 13.2% to maintain the desired oil production rate. Likewise, the reactor volume and the system power requirements also increased by 13.2%.

V. PUBLICATIONS AND PRESENTATIONS

- UCRL-90156 Arthur E. Lewis, Robert L. Braun, and Julio C. Diaz, "Oil Shale Abstract Retorting Processes: A Technical Overview," 17th Oil Shale Symposium, Green Center, Colorado, School of Mines, Golden, CO, April 16-18, 1984.
- UCRL-90221 James F. Carley and Jeanne Swecker Staub, "Mass and Heat Transfer Abstract in Crushed Oil Shale", 17th Oil Shale Symposium, Green Center, Colorado, School of Mines, Golden, CO, April 16-18, 1984.
- UCRL-90234 Otis R. Walton, "Application of Molecular Dynamics to Macroscopic Particles", This paper was presented at the Workshop on Media with Microstructure and Wave Propagation, 24-25 January 1983, Houghton, Michigan.
- 2/22/84 R. W. Taylor, C. J. Morris, and A. K. Burnham, "Nitrogen in Oil Shale, presented at the Ninth Symposium of the Rocky Mountain Fuel Society, Feb. 22-24, 1984, in Salt Lake City, Utah.

VI. VISITORS

- 1/24/84 Ted Bartke, DOE Laramie Project Office - discussions on Oil Shale
- 2/17/84 Ian McFarlane, Fulton Copp (Australian citizens), Ludlow Daniels, (US citizen) consultant, Southern Pacific Petroleum Co. (New York and Australia) subject of discussion - oil shale technology, process modeling, and retorting chemistry.